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# THE EFFECT OF AQUEOUS SOLUTIONS ON COLLOIDAL POWDERS\*

BY J. L. SHERESHEFSKY

Agricultural chemists and geologists have been interested in the property of soils and geologic formations for taking up moisture, and have carried out a number of studies on the quantity of liquid imbibed and on the rate with which the liquid is absorbed.

The methods used in these studies consisted mainly in following the changes in pressure taking place in the cell containing the material, or in the vessel which supplies the liquid. Thus, W. Spring<sup>1</sup> employs a vessel which is provided with a membrane bottom and is connected at the top to a manometer. The material is packed into this vessel and then dipped into water. As the liquid is being taken up, the pressure change which takes place in the cell is followed on the manometer. Joffe and McLean<sup>2</sup> reversed the process by inserting into the material a porous cup filled with water and connected to a manometer. As the colloidal material absorbed the liquid, the pressure in the porous cup diminished. H. Freundlich and W. Sachs<sup>3</sup> improved the latter method by bringing the cell containing the liquid in contact with another vessel of definite thickness containing the colloidal material.

Both methods required accurate temperature control, since they involved changes in gas pressure, and were not suitable for an accurate determination of the total quantity of liquid absorbed. Furthermore, escaping gas bubbles from the pores of the material tend to clog the pores of the membrane in the apparatus of Freundlich and Sachs and thereby introduce inaccuracies in the rate determinations.

It was therefore desirable to devise an apparatus that would eliminate these difficulties and that would also make possible direct measurements of volumes absorbed at various intervals. It was further of interest to investigate the effect of aqueous salt solutions on the rate of sorption of a colloidal clay known to geologists as Jackson shale.

## The Apparatus

The sorptometer as illustrated in Fig. 1 consists of a burette, A, whose smallest division reads .05 cc. To this burette there is connected, by means of the side arm B and the ground joint G, a cup F, containing a porous plate, D. The liquid or solution is introduced into the burette until it fills the apparatus to the top of the porous plate. If air bubbles remain below

\*Contribution from the Chemical Laboratory of Howard University.

<sup>1</sup> Ann. Soc. Geol. Belg., **28** (1901); **29** (1902); Bull. Soc. Bel. Geol., **17** (1903).

<sup>2</sup> Soil Science, **20**, 169 (1925).

<sup>3</sup> Z. physik. Chem., **145A**, 177 (1929).

the plate, they may be removed by suction applied at the mouth of the cup, or by inverting the apparatus and allowing the bubbles to enter the burette. The stop-cock *S* is opened, and excess liquid is allowed to escape until there is no superfluous liquid on the surface of the membrane. This may be easily accomplished by having the level of the liquid in the burette slightly lower than the upper surface of the membrane. The material under investigation is closely packed into cell *C*, which is a glass cylinder provided with a bottom made of perforated filter paper. An ordinary glass plate placed above the

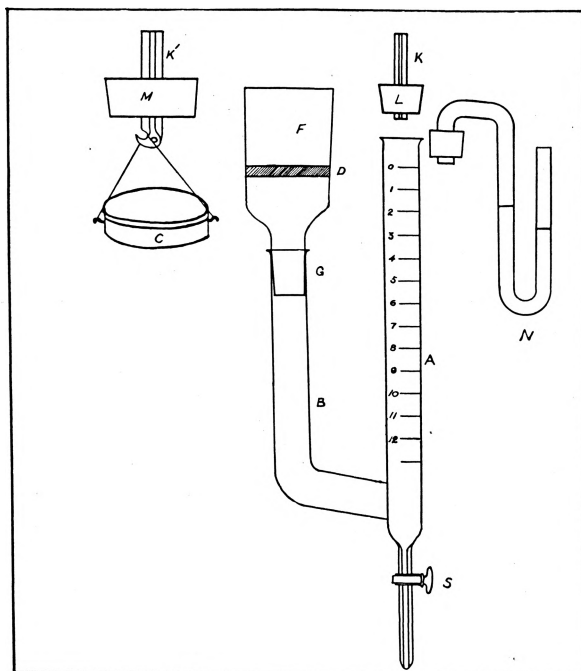


FIG. 1

Sorptometer A-Burette, B-Side Arm, F-Cup, D-Diaphragm, G-Ground Joint, S-Stop-cock, N-Manometer, L and M-Stoppers, C-Cell, K and K'-Capillaries.

colloidal substance served as a top. Stopper *L* with the capillary tube *K* is placed in position to prevent evaporation, and the level of the liquid in the burette is noted. The cell *C* is now picked up by means of the hook on stopper *M* and is placed in cup *F* without having the cell touch the membrane *D*. Now, with stop-watch in one hand, the stopper *M* is put in full position, and timing is begun the moment cell *C* touches the porous plate *D*. The capillary in stopper *M* is to insure atmospheric pressure in the cell, and also to prevent loss of liquid by evaporation. As the liquid is being absorbed by the substance in the cell, the level in the burette drops, and the position of the meniscus is read at desirable intervals.

The maximum drop in the level of the liquid is conditioned by the largest pore in the membrane, and the surface tension of the liquid, since the pressure difference that may be maintained is given by

$$p = 2 \sigma / r$$

where  $p$  is the pressure difference,  $\sigma$  the surface tension, and  $r$  the radius of the largest pore in the membrane. If the liquid level in the burette drops below the minimum level, gas bubbles will appear underneath the membrane. If it is desirable to work with large samples of colloidal material, it is necessary to select a porous membrane with suitably smaller pores, or, when great accuracy in reading the volume of the liquid is not essential, the burette may be changed to one of larger diameter.

The volumetric sorptometer may be easily changed into one which is a combination of both the volume and pressure types. This may be accomplished by inserting manometer N in place of stopper L.

### Experimental and Results

The Jackson shale was ground to 80 mesh, and allowed to come in equilibrium with the moisture in the atmosphere. This was determined by frequent weighing of a given sample until there was no further gain in weight.

The cell C, which was about 3 mm. high and 26 mm. in diameter, was closely packed with a weighed quantity of clay and then carefully lowered into the sorptometer. Readings on the burette were taken at frequent intervals the first thirty or sixty minutes, and then the experiment was allowed to stand overnight. To account for the possible loss of liquid due to evaporation, the apparatus was allowed to stand for twenty-four more hours, and loss of liquid due to evaporation noted. From the total number of hours the experiment was allowed to go and the evaporation correction noted, the total volume imbibed was determined.

The temperature was that of the room, and very seldom varied more than one degree centigrade, since the apparatus was kept under a closed hood protected from air currents. Furthermore, temperature corrections were made, whenever the temperature of the final volume reading differed from that of the first reading by more than one degree.

TABLE I

#### The Rate of Sorption of Distilled Water

| Wt. of Clay  |               | Wt. of Clay  |               |
|--------------|---------------|--------------|---------------|
| 2.3394 grams | Temp. 26° C   | 2.3394 grams | Temp. 26° C   |
| Time in min. | Volume in cc. | Time in min. | Volume in cc. |
| .25          | .40           | 10           | .93           |
| .50          | .45           | 16           | 1.08          |
| 1.0          | .50           | 20           | 1.17          |
| 2.5          | .63           | 70           | 1.55          |
| 5.0          | .76           | 90           | 1.59          |
| 7.0          | .84           | 23 hours     | 1.90          |

In Table I are given the volumes of pure water imbibed at various intervals. In Tables II and III are given the results of experiments with aqueous solutions of sodium chloride and magnesium chloride respectively.

TABLE II

## The Rate of Sorption of Aqueous Solutions of NaCl

| Wt. of Clay<br>in grams   | 2.3385                          | 2.3390 | 2.3383 | 2.3380 | 2.3380 | 2.3385 | 2.3385 |
|---------------------------|---------------------------------|--------|--------|--------|--------|--------|--------|
| Temperature<br>°C         | 25-26                           | 26     | 25.5   | 22     | 22     | 21.5   | 22.5   |
| Normality                 | .001                            | .01    | .05    | .1     | .2     | .3     | .5     |
| Time<br>in min.           | Volume of Solution imbibed, cc. |        |        |        |        |        |        |
| 0                         | 0                               | 0      | 0      | 0      | 0      | 0      | 0      |
| .25                       | .52                             | .51    | .57    | .90    | 1.19   | 1.12   | 1.18   |
| .50                       | .57                             | .57    | .68    | 1.14   | 1.30   | 1.20*  | 1.22   |
| .75                       | —                               | —      | —      | —      | 1.33   | 1.26   | 1.26   |
| 1.00                      | .64                             | .65    | .90    | 1.29   | 1.36   | 1.28   | —      |
| 2.00                      | .72                             | .74    | 1.09   | 1.37   | 1.39   | 1.32   | 1.29   |
| 3.00                      | .77                             | .82    | 1.22   | 1.40   | —      | —      | —      |
| 5.00                      | .87                             | .92    | 1.35   | 1.43   | 1.41   | 1.35   | —      |
| 7.00                      | .95                             | 1.00   | 1.40   | 1.44   | —      | —      | —      |
| 10.00                     | 1.04                            | 1.11   | 1.45   | —      | —      | 1.36   | 1.33   |
| 15.00                     | 1.18                            | 1.25   | 1.49   | 1.45   | 1.43   | —      | —      |
| 20.00                     | —                               | 1.35   | 1.51   | —      | —      | —      | —      |
| 25.00                     | 1.38                            | 1.43   | 1.52   | —      | —      | —      | —      |
| 30.00                     | 1.45                            | 1.48   | 1.52   | —      | —      | —      | —      |
| 40.00                     | 1.53                            | 1.53   | —      | —      | —      | —      | —      |
| 50.00                     | —                               | 1.56   | —      | —      | —      | —      | —      |
| 60.00                     | 1.60                            | —      | —      | —      | —      | —      | —      |
| Final<br>Volume           | 2.13                            | 1.92   | 1.84   | 1.56   | 1.61   | 1.52   | 1.45   |
| Final<br>Time<br>in Hours | 42                              | 43     | 41     | 23     | 41     | 23     | 68     |

\*25 sec.

TABLE III  
The Rate of Sorption of Aqueous Solutions of  $MgCl_2$

| Wt. of Clay<br>in grams | 2.3385                          | 2.3385 | 2.3385 | 2.3385 | 2.3385 | 2.3385 |
|-------------------------|---------------------------------|--------|--------|--------|--------|--------|
| Temperature<br>°C       | 24                              | 26     | 28     | 28-29  | 26     | 28     |
| Normality               | .001                            | .01    | .05    | .1     | .3     | .5     |
| Time in<br>min.         | Vol. of Solution imbibed in cc. |        |        |        |        |        |
| 0                       | 0                               | 0      | 0      | 0      | 0      | 0      |
| .25                     | .50                             | .59    | .90    | .95**  | 1.16** | 1.23   |
| .50                     | .54                             | .66    | —      | 1.27   | 1.28   | 1.28   |
| .75                     | .57                             | .69    | 1.10   | 1.32   | 1.31   | —      |
| 1.00                    | .59                             | .72    | 1.16   | 1.35   | —      | 1.31   |
| 2.00                    | .67                             | .80    | 1.30   | 1.41   | 1.34   | 1.34   |
| 3.00                    | .71                             | .86    | 1.37   | 1.43   | —      | —      |
| 5.00                    | .81                             | .94    | 1.42   | 1.45   | 1.36   | —      |
| 7.00                    | .87                             | 1.02   | 1.45   | —      | —      | —      |
| 10.00                   | .96                             | 1.18*  | 1.49   | 1.47   | —      | —      |
| 15.00                   | 1.09                            | 1.24   | —      | 1.48   | 1.37   | 1.37   |
| 20.00                   | 1.19                            | 1.34   | —      | —      | —      | —      |
| 25.00                   | 1.26                            | 1.40   | 1.52   | —      | —      | —      |
| 30.00                   | 1.34                            | 1.44   | 1.52   | —      | —      | —      |
| 40.00                   | 1.40                            | 1.47   | —      | —      | —      | —      |
| 50.00                   | 1.45                            | —      | —      | —      | —      | —      |
| 60.00                   | —                               | —      | —      | —      | —      | —      |
| Final<br>Volume         | 1.86                            | 1.84   | 1.63   | 1.57   | 1.51   | 1.39   |
| Final Time<br>in Hours  | 67                              | 45     | 42     | 67     | 42     | 25     |
| *12 min.                | **10 sec.                       |        |        |        |        |        |

The results obtained are rather interesting. As it will be observed, the rate of sorption increases with concentration, reaches a maximum, and then decreases. This is true for both the sodium chloride and the magnesium chloride solutions. The accelerated rate of sorptions as related to concentrations is illustrated in Fig. 2, where curve H is that of pure water, and B, C and D are those of .001 N, .05 N, and .2 N sodium chloride solutions respectively.

It will be observed also, by comparing Tables II and III, that the rate of sorption at equal concentrations is greater for magnesium chloride than for sodium chloride. Curves A and B represent the rates of sorption of .01 N sodium chloride and magnesium chloride respectively, and C and D are the curves for .05 N solutions of sodium chloride and magnesium chloride respectively.

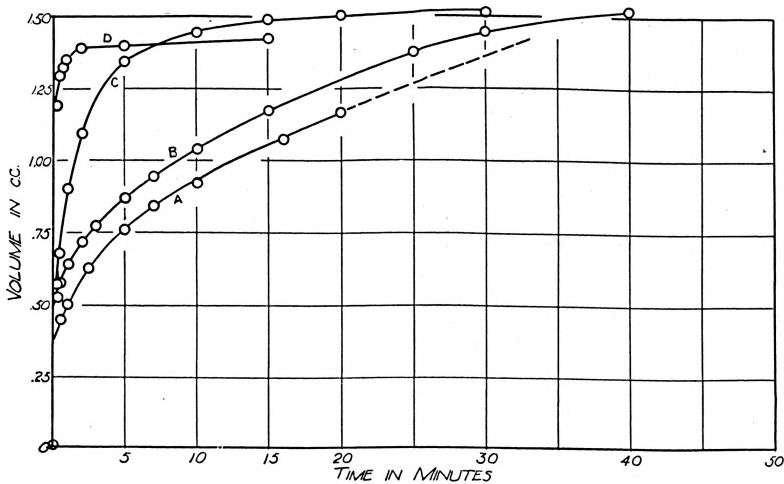


FIG. 2

The Imbibition of NaCl Solutions by Jackson Shale; A, distilled water; B, .001 N NaCl; C, .05 N NaCl; D, .2 N NaCl.

Furthermore, it is to be noted that the final volume imbibed is also dependent upon the concentration. In the case of sodium chloride, the volume rapidly increases, reaches a maximum, and then decreases quite gradually. In the case of magnesium chloride solutions no maximum is observed, as shown in Fig. 4.

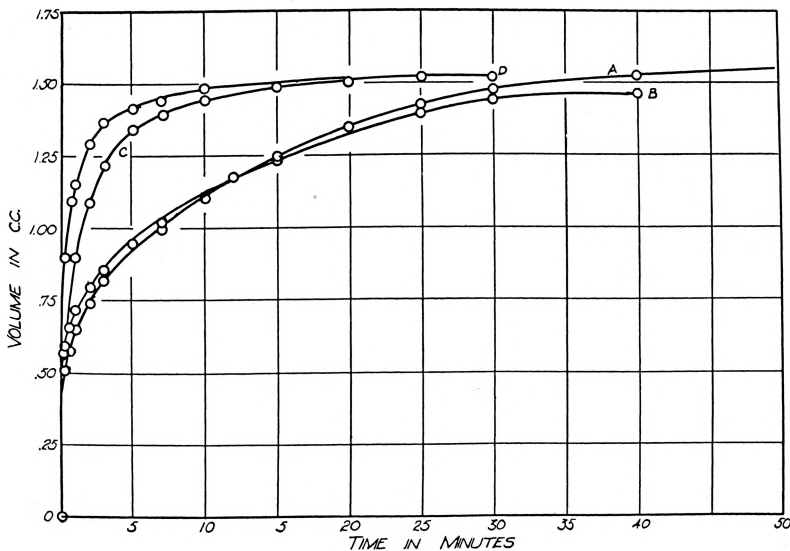


FIG. 3

The Imbibition of NaCl and MgCl<sub>2</sub> by Jackson Shale at equimolar Concentrations; A, .01 N NaCl; B, .01 N MgCl<sub>2</sub>; C, .05 N NaCl; D, .05 N MgCl<sub>2</sub>.

The behavior of the clay towards electrolyte solutions as described above is so similar to colloidal behavior that Freundlich and Sachs<sup>1</sup> suggested it to be completely analogous to the behavior of suspensions. Assuming that the clay consists of aggregates of fine colloidal particles, the electrolyte solution tends to discharge them and cause their coalescence. As a result larger pores are formed in the clay, which is responsible for the increased rate of sorption. The maximum rate would therefore correspond to maximum coagulation. The maximum for magnesium chloride was about 0.2 N, and for sodium

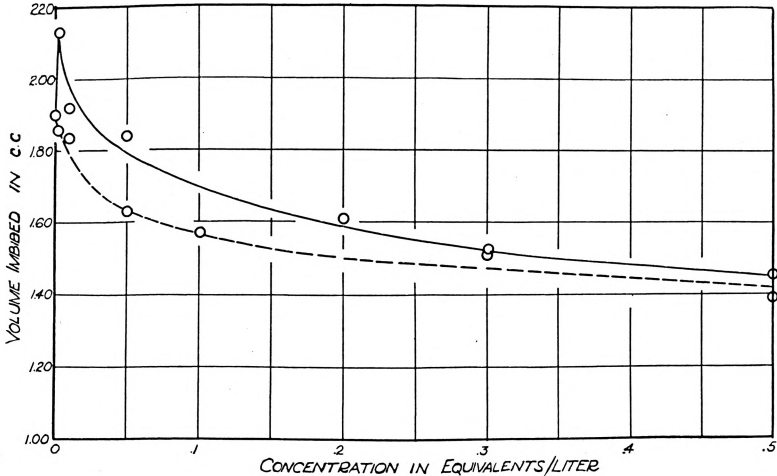


FIG. 4

Imbibition of NaCl and MgCl<sub>2</sub> Solutions at Various Concentrations; full line, NaCl Solutions; broken line, MgCl<sub>2</sub> Solutions.

chloride about 0.3 N. Higher concentrations, because of the greater viscosity, tend to retard the rate of sorption.

The total volume imbibed seems to be connected with the phenomenon of swelling. The imbibition of .001 N and .05 N sodium chloride solutions was accompanied by noticeable swelling of the total mass of clay. With the more concentrated solutions of sodium chloride and with all concentrations of magnesium chloride no swelling was observed. On the contrary, the sorption in the latter cases was accompanied by a contraction in volume.

### Summary

Methods of measuring rate of sorption of colloidal powders are reviewed. The construction of a volumetric sorptometer is described.

The effect of solutions of sodium chloride and magnesium chloride on the rate of sorption of Jackson shale is studied.

The mechanism of sorption of colloidal powders is discussed.

Washington, D. C.  
November, 1931.

<sup>1</sup> Loc. cit.